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Behaviour of triazine herbicides and their hydroxylated and dealkylated metabolites on a propazine-imprinted polymer

Comparative study in organic and aqueous media

R. Carabias-Martínez [*], E. Rodríguez-Gonzalo, E. Herrero-Hernández

Departamento de Química Analítica, Nutrición y Bromatología, Facultad de Química, Universidad de Salamanca, 37008 Salamanca, Spain

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Abstract

A molecularly imprinted polymer (MIP) obtained by precipitation polymerization with methacrylic acid as functional monomer and propazine as template was tested as a sorbent for the solid phase extraction of chloro- and methylthio-triazines and some of their dealkylated and hydroxylated metabolites. In order to confirm the interaction between the functional monomer and the template, ^{1}H NMR (CD_2Cl_2) analyses were made. It was observed that the hydrogen and/or nitrogen of the amino group of the propazine were involved in the formation of hydrogen bonds with the functional monomer.

The possibilities offered by the propazine-MIP for the extraction of triazine and derivatives were studied in organic and aqueous media and different types of behaviour were observed. From organic medium, selective extractions of chloro- and methylthio-triazines were obtained after optimization of the extraction process, with recoveries higher than 75% in both cases. However, the hydroxylated metabolites were not retained on the propazine-MIP in organic medium.

In aqueous medium, the chloro-triazines and the dealkylated chloro-metabolites were retained on the propazine-MIP by specific interactions, the recoveries obtained being a function of their polarity. Regarding the hydroxylated metabolites, these are retained on the propazine-MIP through non-specific hydrogen-bridge interactions. The methylthio-triazines undergo poor molecular recognition in this medium.

Keywords: Molecularly imprinted polymers; Precipitation polymerization; Triazine herbicides; Dealkylated and hydroxylated metabolites

1. Introduction

Triazine herbicides are some of the more commonly used in Europe as selective pre- and post-emergence herbicides for the control of broadleaf and grassy weeds in many agricultural crops. Their prolonged use involves the risk of their retention in crops and soils from which in turn, due to washing and leaching processes, these substances pass to surface and ground waters [1,2]. In previous work [3,4] evaluating these herbicides in an agricultural zone close to the City of Salamanca (Spain), we observed that surface and ground water samples contained levels of atrazine, terbutryne and deethylatrazine (DEA) above 0.1 $\mu g\,L^{-1}$.

In water, parent triazine herbicides are subject to various biotic and abiotic degradation processes such as photolysis, oxidation, hydrolysis and biodegradation, leading to the dealkylation of amine groups, dechlorination, hydroxylation, deamination, etc. [5,6]. For example, with respect to atrazine the main degradation products in water are the dealkylated chloro-metabolites: deethylatrazine (DEA) and deisopropylatrazine (DIA) [7,8].

Analytical methods for the determination of pollutants in environmental samples usually require a preconcentration step. Solid-phase extraction (SPE) is a powerful tool for the pretreatment of environmental waters and other kind of matrices, such as biological fluids, plant tissue culture and forensic samples. The main problem associated with SPE with ordinary stationary phases is its low selectivity. More selective sorbents have been developed, based on molecular recognition mechanisms. These include immunosorbents that use selective antigen–antibody interactions and molecularly imprinted polymers (MIPs).

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[*] Corresponding author. Fax: +923 294 574.
E-mail address: rcm@usal.es (R. Carabias-Martínez).

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Different authors have employed MIPs to extract triazines from different matrices such as water [9–11], vegetable extracts [12], beef liver [13], urine, apple extract [14] and soil [15] and also an atrazine sensor based on MIP modified electrodes [16] has been developed. Most of these works attempt to study the retention of parent compounds (chloro- and methylthio-triazine herbicides) using MIPs obtained by bulk polymerization. Although in some cases dealkylated chloro-metabolites have also been included [11,17], few works have addressed the behaviour of hydroxylated metabolites. Only the works of Chapuis et al. [15,18] included hydroxyterbutylazine among the target analytes for retention studies on a terbutylazine-MIP obtained by bulk polymerization. As far as we are aware, there are no reports that have addressed the retention behaviour of N-dealkylated hydroxy-metabolites.

The aim of this work was to check the possibilities of MIPs prepared by precipitation polymerization for the molecular recognition of different triazinic derivatives (chloro- and methylthio-triazines and some of their hydroxylated, dealkylated and dealkylated hydroxy-metabolites) when the sample passing through the sorbent is organic or aqueous. The mechanism of the retention in both media was studied and the results were compared with those reported by other authors with MIPs obtained by bulk polymerization.

The selectivity of the MIP for the specific retention of these metabolites in organic and aqueous solutions was assessed against non-triazine herbicides in frequent use: lenacil, chlorsulfuron, isoproturon and linuron.

2. Experimental

2.1. Chemicals

The herbicides and the metabolites were obtained from Dr. Ehrenstorfer (Augsburg, Germany) and were used without further purification. The triazine compounds are listed in Table 1. Other herbicides were: *chlorsulfuron* (Cls) 1-(2-chlorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea CAS RN [64902-72-3]; *isoproturon* (Ipn) 3-(4-isopropylphenyl)-1,1-dimethylurea CAS RN [34123-59-6]; *linuron* (Lin) 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea CAS RN [330-55-2] and *lenacil* (Len) 3-cyclohexyl-1,5,6,7-tetrahydrocyclopentapyrimidine-2,4(3H)-dione, CAS RN [2164-08-1].

Stock solutions of each herbicide and metabolite were prepared in acetonitrile at 500 μg mL^{-1} except in the case of the hydroxylated metabolites which were prepared in acetonitrile–0.1 M hydrochloric acid (80:20, v/v) at a concentration of 200 μg mL^{-1}.

Methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA) and 2,2′-Azobis(2-methyl-propionitrile) (AIBN) were obtained from Acros Organics (Geel, Belgium). The organic solvents, toluene, dichloromethane, acetonitrile and methanol were of HPLC grade (Merck) and were used as received. Ultra-high quality UHQ water (purity 18.2 MΩ cm at 25 °C) was obtained with an Elgastat UHQ water purification system (Elga Ltd., Bucks, UK). All other chemicals were of analytical reagent grade.

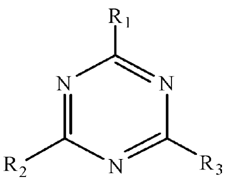
2.2. Synthesis and characterization of the imprinted polymer

The procedure followed to obtain the MIP by precipitation was as follows: the template, propazine (1 mmol) and the functional monomer, MAA (4 mmol), were added to a glass tube and after 5 min EGDMA (20 mmol), toluene (30 mL) and AIBN (0.2 mmol) were added. The solution was degassed with nitrogen for 5 min and the tubes were closed and sealed under this atmosphere. Microspheres were obtained by precipitation polymerization in a water bath at 60 °C for 10 h with stirring at 350 rpm. The resulting microspheres were washed twice with acetone to remove the fine particles. Template was removed by Soxhlet extraction with a methanol:acetic acid (9:1, v/v) mixture until no template was found in the washing solution (analyzed by HPLC-DAD UV).

Blank polymers or non-imprinted polymers (NIP) were prepared in the same way but without the addition of the template to the polymerization mixture.

Characterization of the imprinted polymer was made by nitrogen sorption and scanning electron microscopy measurements. Nitrogen sorption measurements were performed on a Gemini 2375 (Micromeritics Instrument Corporation, Norcross, GA) at the *Department of Inorganic Chemistry* (University

Table 1
General structure and some properties of triazine herbicides and metabolites considered in this work

	Compounds	R_1	R_2	R_3	$\log K_{ow}$[a]	pK_a
	Deisopropylhydroxyatrazine (DIHA)	–OH	$-NH_2$	$-NH-CH_2-CH_3$	−0.1	4.65
	Deethylhydroxyatrazine (DEHA)	–OH	$-NH-CH(CH_3)_2$	$-NH_2$	0.2	4.57–4.75
	Deisopropylatrazine (DIA)	–Cl	$-NH_2$	$-NH-CH_2-CH_3$	1.15	1.30–1.58
	Deethylatrazine (DEA)	–Cl	$-NH-CH(CH_3)_2$	$-NH_2$	1.52	1.30–1.65
	Hydroxyterbutylazine (HT)	–OH	$-NH-C(CH_3)_3$	$-NH-CH_2-CH_3$	–	5.2
	Simazine (Smz)	–Cl	$-NH-CH_2-CH_3$	$-NH-CH_2-CH_3$	2.18	1.65
	Atrazine (Atz)	–Cl	$-NH-CH(CH_3)_2$	$-NH-CH_2-CH_3$	2.5	1.68
	Propazine (Ppz)	–Cl	$-NH-CH(CH_3)_2$	$-NH-CH(CH_3)_2$	2.93	1.85
	Terbutylazine (Tbz)	–Cl	$-NH-C(CH_3)_3$	$-NH-CH_2-CH_3$	3.21	2.00
	Prometryn (Pmn)	$-SCH_3$	$-NH-CH(CH_3)_2$	$-NH-CH(CH_3)_2$	3.51	4.05
	Terbutryn (Tbn)	$-SCH_3$	$-NH-C(CH_3)_3$	$-NH-CH_2-CH_3$	3.65	4.38

[a] $\log K_{ow}$: *n*-octanol–water partition coefficients, defined as the ratio of the equilibrium concentrations of a dissolved substance in two immiscible solvents.